

Mathematical Modeling of the Impedance of Single and Multi-tube AMTEC Units

V. B. Shields, R. M. Williams, M. A. Ryan, R. Cortez, M. L. Homer,
A. K. Kisor, K. Manatt

*Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive, Pasadena, CA 91109
(818) 354-9506, Virgil.B.Shields@jpl.nasa.gov*

Abstract. AMTEC power systems are designed for use on extended space missions. During the lifetime of such missions the power available for the spacecraft will depend on the degradation of the system performance. Development of a tool that allows monitoring of the system degradation will provide an aid in determining the condition of the power source. Since the power output is a function of the impedance across the BASE tube and electrodes, monitoring its variation can provide an understanding of the internal changes within the AMTEC unit. A lumped element impedance model is being developed for a single cell and a six cell AMTEC unit. The analysis was performed using the symbolic analysis software program, Mathematica. The model examines the cathode-BASE-anode impedance by allowing the BASE and the electrode-BASE interfaces to be depicted as a combination of resistances, Warburg impedances and pseudo capacitances (i.e. constant phase elements). The model results are compared with operational measurements from single and six tube AMTEC units tested for more than 1000 hours.

INTRODUCTION

Alkali Metal Thermal to Electric Converter (AMTEC) power units are designed to function during extended space missions and provide power at an optimal level. During that time the internal components undergo degradation resulting from interactions between the various materials that comprise the AMTEC unit at the relatively high operational temperatures. These degradation mechanisms can affect the overall performance of the unit by reducing the output power below expected levels or in a worst case causing a failure of the AMTEC. One potential area of concern is the conduction path across the AMTEC cells that provided the key part of the AMTEC device. The AMTEC unit is composed of a number of cells connected in series that provide power resulting from the conduction of ions from an inner high pressure sodium reservoir through a layer of beta" (i.e. beta double prime) alumina solid electrolyte (BASE). On either side of this BASE layer is an electrode; on the inner high pressure side is the anode while the outer surface is coated with conductor that functions as a cathode. Changes in this conduction path will affect the current flow and impair the performance of the cell.

Several known degradation mechanisms are grain growth in the thin film electrodes deposited on the inner and outer BASE surface, interactions between the sodium working fluid and the electrodes and BASE material that alter the composition; and contamination of the electrode surface from materials leached from the other components of the AMTEC unit that are transferred to the electrode surfaces and possibly into the pores of the BASE by the sodium as it circulates throughout the unit. The effects of these mechanisms on the cell performance can be determined by measurements of the R_{act} (apparent charge transfer resistance) (Williams et al, 1990a; 1990b) across the anode-BASE-cathode layer. Electrochemical Impedance Spectroscopy (EIS) is a technique useful for measuring the impedance as a function of frequency and providing a way to determine ongoing changes within the AMTEC cell (Ryan et al, 1991).

Long term tests conducted on AMTEC units comprised of both single cells and multiple cells have provided a way of comparing the impedance of a single cell electrode-BASE conduction path to that of a more typical unit that has

multiple cells. In other words, impedance measurements on single cell AMTEC units will potentially allow the deconvolution of a single electrode-BASE interface from that of the multiple interfaces in a typical AMTEC and allow a determination as to what degree degradation is occurring.

EXPERIMENTAL

AMTEC units designed to contain single cells and six cells were fabricated by Advanced Modular Power Systems Inc. (AMPS) were life tested at JPL (Shields et al, 2000). Various electrical measurements were made during operation including impedance as a function of frequency using EIS. The frequency range for the measurements generally extended from about 65000 Hz down to 0.05 Hz. The results presented in this paper will be for measurements made under open circuit voltage conditions. A single cell unit denoted as ST1 was tested for more than 1000 hours. The ST1 AMTEC unit contained a single cell and was designed to allow analysis of the effects of a single cathode-BASE-anode conduction path. The impedance was measured at external cathode and anode connections external to the unit. The impedance measurements at 145 hours and 1050 hours are shown in Figure 1. The results are presented as Nyquist plots showing the reactance (i.e. the imaginary part of the impedance, $\text{Im}(Z)$)

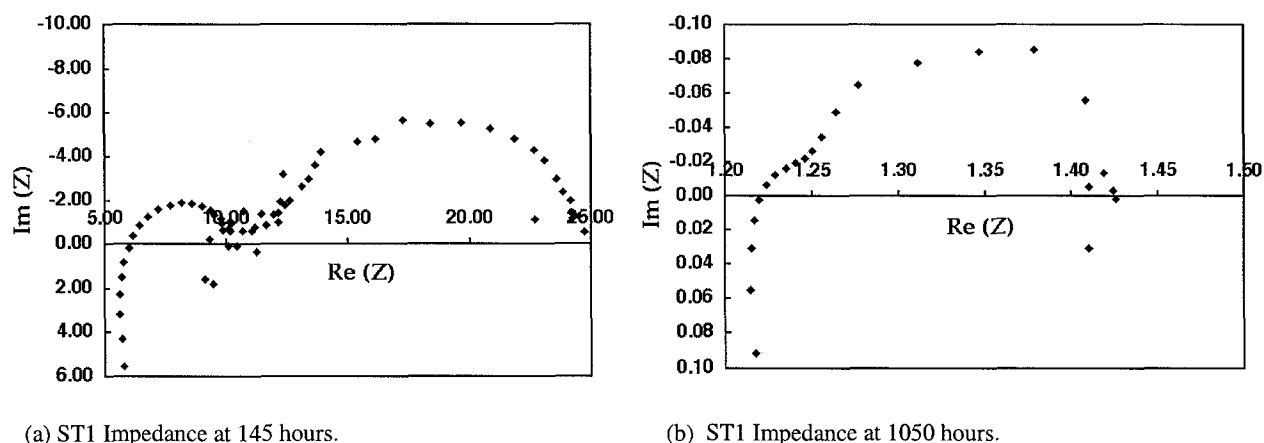


Figure 1. Variation in a single cell AMTEC unit impedance over about 1000 hours of testing.

plotted versus the resistance component (i.e. the real part of the impedance, $\text{Re}(Z)$). The upper regions of each graph in Figure 1 result from capacitive impedance contributions while the lower portion are due to inductive effects. The measured R_{act} is the resistance value where the curves cross the horizontal axis at the furthest point or lowest frequency in the right part of the graphs, minus the series resistance, R_{ser} , where the curves cross the real axis at the left side of the graph; at the higher frequency. The curves vary from left to right with frequency. The highest frequency contributions are at the leftmost part of the graphs extending to the lowest frequency contributions at the rightmost portion of the curves. In each case there are two characteristic loops that are related to paralleled resistance-capacitance circuit effects in the conduction path. The principal changes in the plots appear to be due to the resistance and capacitance changes as opposed to inductive ones. The loops are observed to decrease in size with time of operation along with a corresponding decrease in the R_{act} . The overall R_{act} which corresponds to the size of the loops is expected to decrease substantially as the cell's open circuit voltage, OCV, decreases, whatever the mechanism for OCV decrease. The detailed change in the impedance plot, however, can provide more specific information about the degradation mechanism. Also apparent is a shift in the relative positions and size of the loops.

Figure 2 shows the results for a six cell AMTEC denoted as Creare 2 due to its high efficiency cold end sodium condenser fabricated by Creare Inc., incorporated into the AMPS designed AMTEC unit. The Creare 2 AMTEC unit contained six cells connected in series with the cathode and anode electrodes for each cell connected internal to the unit. The impedance measurements were made at external cathode and anode connections located at the opposite ends of the six series string of cells. The Creare 2 AMTEC unit was operated for more than 500 hours. The impedance at 49 hours shows more complexity than those of the single cell ST1 unit. This added structure is likely due to parallel impedance effects between multiple adjacent series cells not present in the single cell unit. In

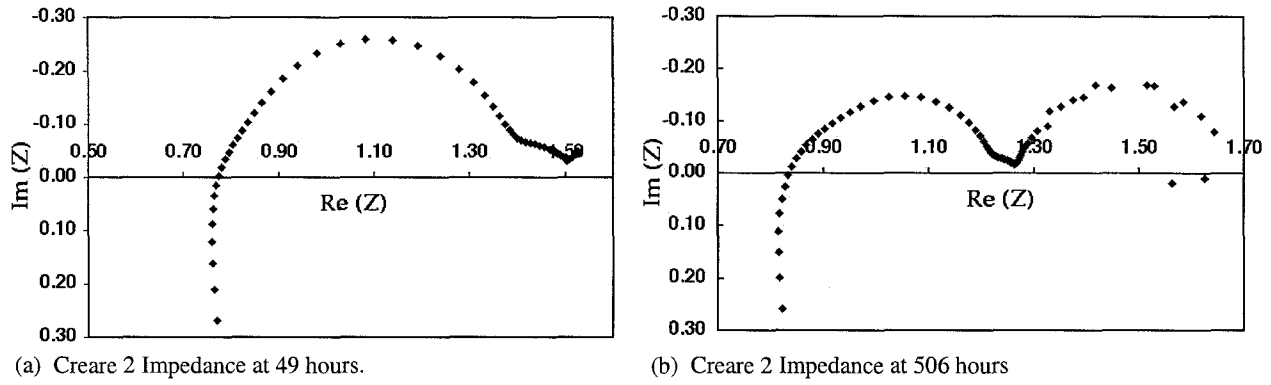


Figure 2. Variation in a six cell AMTEC unit impedance over 500 hours of testing.

addition, very low frequency measurements (i.e. down to 0.0004) conducted near the end of testing of the Creare 2 unit showed more structure in the form of an additional capacitive loop similar to the higher frequency one. As with the ST1 unit the sizes of the loops are observed to decrease in size as a time of operation increases.

MODELING RESULTS

The impedance model in its present form depicts the cathode-BASE-anode conduction path as having five regions; cathode, cathode-BASE interface, BASE, BASE-anode interface, and anode. The model depicts the electrode-BASE interfaces and the BASE as paralleled pseudo capacitances in the form of constant phase elements and non-linear pseudo resistances formed from series ohmic resistances and Warburg impedances (Tomkiewicz, 1993; Bisquert, 1998). The constant phase elements are assumed to have the form $(j\omega C)^{-n}$ where $j = \sqrt{-1}$, $0 < n < 1$, ω is the applied frequency, and C is an adjustable constant that represents a pure capacitance for $n=1$ (Bard, 1980). The use of constant phase elements which deviate from pure capacitances allow incorporation of frequency dispersion effects in the diffusion through the various conduction regions. The incorporation of Warburg impedance allows for the proper modeling of the pseudo or non-linear resistance effects due to variations in mass transfer resistance related to sodium diffusion through the electrode. The model incorporates the Warburg impedance effects in the form $\sigma(\omega^{-\frac{1}{2}})$, where σ is an adjustable multiplicative factor (Bard, 1980).

The present version of the impedance model depicts the cathode-BASE-anode cell interface as shown in Figure 3. In this initial model the conduction path across the BASE is modeled as a parallel non-linear resistance and a pseudo capacitance in each of three middle regions composed of the cathode-BASE interfacial region, BASE and BASE-

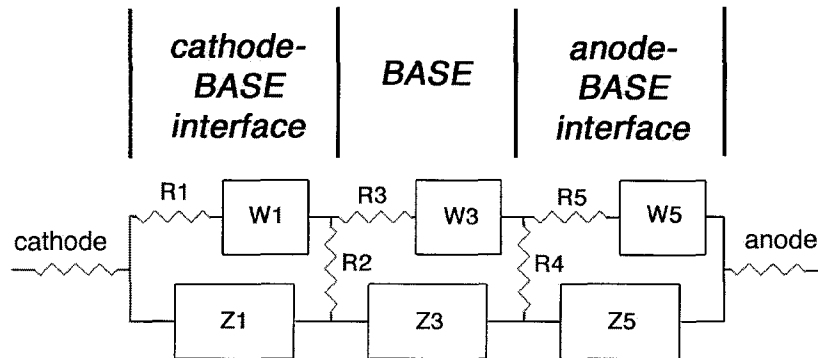


Figure 3. Diagram of the Lumped Element Model for the AMTEC Unit.

anode interfacial region. Surface conduction along the electrode-BASE interface is modeled as a pure ohmic resistance. The electrodes are modeled simply as ohmic resistances. Although some inductance contribution is apparent from the impedance measurements on operational cells and electrode-BASE interfaces, those effects are not dominant compared to the changes in the resistive and capacitive contributions so are not included in the present version of this model.

Preliminary analyses have attempted to match the impedance patterns produced by the model with the actual measured performance of the single cell ST1 AMTEC unit. After matching the characteristics of the initial state of the unit, the change in parameters required to adjust the model to the later operational state were expected to provide insight into which are of principal importance in the degradation process.

Figure 4 shows the modeling results for the initial state of the ST1 AMTEC unit at 49 hours. Only the capacitive and resistive contributions are incorporated as opposed to the inductive effects. Also shown in Figure 4 are the results for the 1050 hour measurements.

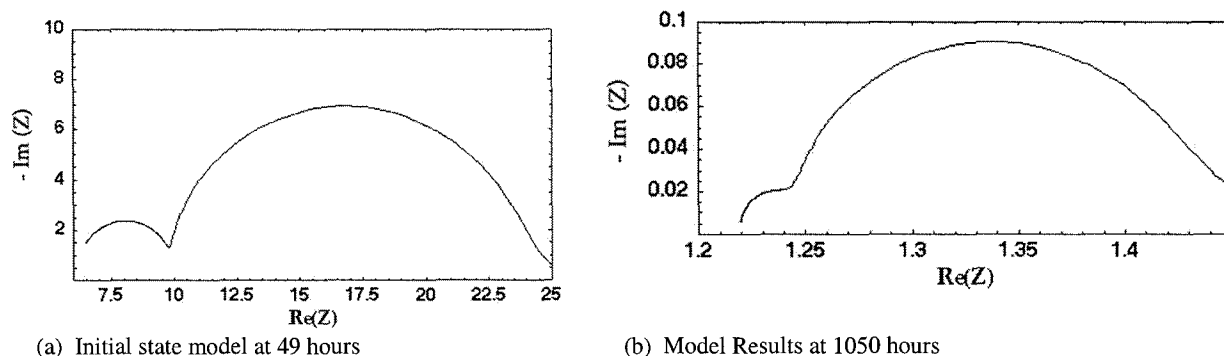


Figure 4. Models Results for the ST1 AMTEC Unit.

The principal changes incurred in going from the initial state of the model to what is depicted at 1050 hours are an overall reduction in the ohmic resistance contributions affecting conduction perpendicular to the interfaces. Changes in the resistance affecting conduction along the electrode-BASE interfaces show no significant affects. To reach the 1050 hour modeling state a decrease in the cathode-BASE and the BASE-anode resistance of nearly 200 times was incorporated. In addition there was approximately a factor 5 decrease in the electrode resistance. The smoothing of the interface between the two loops resulted from an increase in the capacitive impedance of the BASE-anode interface.

CONCLUSION

Preliminary results indicate that the changes in the impedance over approximately 1000 hours of operation for the single cell AMTEC was principally due to a reduction in the ohmic resistances of all of the interfaces and the electrodes. One mechanism which would allow this sort of change is an increase in the sodium activity at the cathode, which would in turn decrease the interface's charge transfer resistance, and would also be consistent with the formation of sodium leaks or internal discharge modes. Capacitive effects are also observed to play a role in changing the relative structure of the impedance loops in the Nyquist plots. However due to the number of variables contained within the model more analysis needs to be done to improve confidence in our understanding of the relative contributions of the impedance elements leading to definite degradation mechanisms. In addition work is just starting on modeling the processes involved in series inter-linked cells that exist in complete AMTEC units.

ACKNOWLEDGMENTS

The research reported in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. Research was supported by NASA Code S.

REFERENCES

- Bard, A. J., and Faulkner, L. R., *Electrochemical Methods*, John Wiley & Sons, New York, 1980, pp. 323.
- Bisquert, J., Garcia-Belmonte, G., Bueno, P., Longo, E., Bulhoes, L. O. S., "Impedance of Constant Phase Element (CPE)-blocked Diffusion in Film Electrodes", *J. Electroanalytical Chem.*, Vol. 452, 229-234 (1998).
- Ryan, M. A., Jeffries-Nakamura, B., O'Connor, D., Underwood, M. L., Williams, R. M., "AMTEC Electrode Morphology as Studied by Electrochemical Impedance Spectroscopy and Other Techniques", Proceedings of the Symposium on High Temperature Electrode Materials and Characterization, D. D. Macdonald and A. C. Khandkar, editors, The Electrochemical Society, Proceedings Vol. 91, 6, p. 115 (1991).
- Shields, V. B., Kisor, A. K., Fiebig, B., Williams, R. M., Ryan, M. A., Homer, M. L., "Metallurgical Examination of an AMTEC Unit", Proceedings of the Seventeenth Symposium on Space Nuclear Power and Propulsion, M. S. El-Ghenk, ed., American Institute of Physics, (2000).
- Tomkiewicz, M., "Impedance of Composite Media", *Electrochimica Acta.*, Vol. 38, No. 14, 1923-1928 (1993).
- Williams, R. M., Loveland, M. E., Jeffries-Nakamura, B., Underwood, M. L., Bankston, C. P., Leduc, H., Kummer, J. T., "Kinetics and Transport at AMTEC Electrodes I. The Interfacial Impedance Model", *J. Electrochem. Soc.*, **137**, 1709-1715 (1990a).
- Williams, R. M., Jeffries-Nakamura, B., Underwood, M. L., Bankston, C. P., Kummer, J. T., "Kinetics and Transport at AMTEC Electrodes II. Temperature Dependence of the Interfacial Impedance of Na_{g} /Porous Mo/Na- β Alumina", *J. Electrochem. Soc.*, **137**, 1716-1722 (1990b).